Short Communication

Synthesis and Crystal Structure of the Copper(II) Complex of 1-Methyl-4,7,10-(2-pyridylmethyl)-1,4,7,10-tetraazacyclododecane (L), [CuL]²⁺

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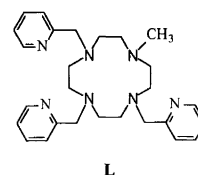
The coordination properties toward metal ions of macrocycles bearing pendant donor groups from the macrocycle skeleton have recently attracted much interest, mainly as the study of such systems may provide the basis for a better understanding of the metal environment in some metalloenzymes and metalloproteins.[1,2] Recently some reports have indicated that functionalized macrocycles containing pendant arms can form stable complexes with transition metals and exhibit functional properties. These types of macrocycles can bond to metal ions forming 1:1 or 1:2 molar ratio complexes.[2–5]

1,4,7,10-Tetraazacyclododecane (cyclen) appended with four pyridine groups through methylene chains and its transition metal complexes have been reported.[6,7] The octadentate ligand can bond to transition metals and lanthanides, forming stable complexes, and can exhibit interesting structure features and functional properties. This type of ligand, macrocycles bearing pendant donor groups from the macrocycle skeleton, held considerable interest for us, and has led us to synthesize a new relative ligand [L: 1-methyl-4,7,10-(2-pyridylmethyl)-1,4,7,10-tetraazacyclododecane] and its complexes with a transition metal, so as to define further the relationship between structural features and pendant donor groups. We report herein the synthesis and structural features of the copper(II) complex with L.

Experimental

Preparation of the complex [CuL] · (ClO₄)₂. A single crystal of the title complex suitable for X-ray analysis was obtained by mixing a 1:1 molar ratio of Cu(ClO₄)₂

L

(8.1 mg, 0.022 mmol) and L (10 mg, 0.022 mmol) in methanol–acetonitrile (1:1) with stirring for ca. 30 min. The reaction mixture was filtered, and a blue single crystal was obtained from the filtrate by slow evaporation of the solvent. Yield: 50% (7.9 mg). IR (KBr pellet): 2849, 1609, 1593, 1570, 1479, 1444, 1307, 1097 (broad and strong), 1023, 957, 807, 624 cm⁻¹.

Crystallographic studies. A blue crystal (approximately $0.2 \times 0.3 \times 0.4$ mm) of the title complex was mounted on an Enraf-Nonius CAD-4 diffractometer, equipped with a graphite crystal monochromator. Determination of the unit cell and data collection were performed with Mo Kα radiation ($\lambda = 0.71073$ Å). Unit-cell dimensions were obtained by least-squares refinements using 25 reflections in the range $9.33 < \theta < 12.07°$. The intensities of the reflections were measured in the $\omega/2\theta$ ($\theta_{max} = 27°$) scan mode at room temperature. From 2431 independent reflections, 1978 reflections with $I \geqslant 3\sigma(I)$ were considered to be observed, and were used in the succeeding refinement. The structure was solved by direct methods using the SHELXS-86 program[8] and refined on F by a full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms using SHELXL-93.[9] Unweighted and weighted (unit weights for all observed reflections) agreement factors are 0.072 and 0.074.

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Crystal parameters and refinement results are given in Table 1. Atomic coordinates are listed in Table 2, and selected bond lengths and angles are presented in Table 3.

Results and discussion

X-Ray crystal and molecular structure. The structure of the title compex consists of discrete monomeric $[CuL]^{2+}$ cations separated by perchlorate anions. Figure 1 shows a perspective view of the cationic entity. In the complex the copper(II) atom can be considered as six-coordinated [with N(1), N(2), N(3), N(4), N(11) and N(21)]. The macrocyclic molecule (L) acts as a hexadentate ligand through its four basal macrocyclic nitrogen atoms and its nonadjacent two pyridine nitrogen atoms. The pyridine nitrogens occupy the remaining pair of *cis* positions in the coordination polyhedron. The other pendant pyridine remains uncoordinated apart from the Cu^{II} center.

The coordination geometry about the copper atom can be described as an elongated or strongly distorted octahedron, where N(2) and N(4) occupy the axial position [N(2)–Cu–N(4): 124.9°]. The Cu–N distances of the pyridyl groups and Cu–N(1), Cu–N(2) of macrocycle nitrogens are 2.035–2.144 Å, the normal Cu–N distance, but for Cu–N(3)and Cu–N(4) they are 2.331 and 2.828 Å, respectively, being longer than the normal Cu–N distance, indicating weak coordination of N(3) and N(4). The Cu–N(4) distance is large and can be considered as semi-coordinated.[10] If the semi-bond is ignored, the coordination geometry of the remaining CuN_5 [N(1), N(2), N(3), N(11) and N(21)] can be considered as intermediate between a trigonal bipyramid (TBP) and a square pyramid (SPY). According to the τ-parameter, defined by Addison *et al.*[11] as $\tau = (\beta - \alpha)/60$ to quantify the geometry, $\tau = 0$ for SPY and $\tau = 1$ for TBP. Table 3 shows $[CuL]^{2+}$ to have a τ-value of 0.43 [in our case, $\alpha = N(3)$–Cu–N(11) and $\beta = N(1)$–Cu–N(21)], indicating a strong distortion of the

Table 1. Crystallographic data for $[CuL]^{2+}$.

Formula	$C_{27}H_{37}N_7Cl_2O_8Cu$
M_r	722.08
Crystal colour	Blue
Space group	$P2_1cn$
$a/\text{Å}$	10.175(2)
$b/\text{Å}$	15.191(3)
$c/\text{Å}$	20.790(4)
$V/\text{Å}^3$	3213(1)
Z	4
$D_c/\text{g cm}^{-3}$	1.492
μ/cm^{-1}	9.037
$F(000)$	1500
No.of measured reflections	2740
No. of independent reflections	2431
No. of observed reflections $[I > 3(I)]$	1978
R	0.072
Rw	0.074
$(\Delta/\sigma)_{max}$	0.415
S	2.78
Max. residual peak/$e\,\text{Å}^{-3}$	0.64

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$).[a]

| Atom	X	Y	Z	U(eq)
Cu(1)	8969(4)	2194(1)	7459(1)	45(1)
Cl(1)	13800(5)	435(2)	7670(2)	52(1)
Cl(2)	5301(5)	1082(2)	4758(2)	60(1)
O(11)	13586(13)	1285(5)	7944(7)	131(2)
O(12)	12914(11)	−196(8)	7901(6)	88(2)
O(13)	13710(13)	443(8)	6985(6)	111(2)
O(14)	15132(12)	150(8)	7863(6)	93(2)
O(21)	5058(13)	1329(9)	4128(7)	126(2)
O(22)	6224(15)	417(12)	4744(9)	177(2)
O(23)	4140(19)	948(16)	5098(13)	342(2)
O(24)	6158(17)	1687(14)	5034(11)	256(2)
N(1)	7522(9)	2492(7)	8123(6)	51(1)
N(2)	7413(11)	2346(9)	6773(7)	75(1)
N(3)	9039(12)	791(6)	7006(4)	53(1)
N(4)	9103(11)	849(7)	8397(5)	58(1)
C(1)	6209(12)	2450(10	7827(8)	67(1)
C(2)	6320(12)	2840(10)	7155(9)	84(1)
C(3)	6922(13)	1421(9)	6613(8)	72(1)
C(4)	8139(13)	892(9)	6427(8)	78(1)
C(5)	86519(13)	34(8)	7401(7)	72(1)
C(6)	9281(13)	−9(8)	8037(7)	66(1)
C(7)	7756(13)	951(9)	8602(7)	66(1)
C(8)	7516(13)	1906(10)	8741(8)	78(1)
C(9)	7713(14)	2810(9)	6181(8)	75(1)
C(10)	7912(12)	3381(9)	8328(7)	60(1)
C(11)	9308(11)	3379(7)	8492(6)	45(1)
C(12)	9894(13)	3870(10)	8999(7)	67(1)
C(13)	11258(14)	3741(10)	9113(7)	83(1)
C(14)	11954(12)	3239(8)	8719(6)	56(1)
C(15)	11377(12)	2809(9)	8221(7)	59(1)
N(11)	10041(10)	2886(6)	8113(5)	43(1)
C(20)	10447(13)	714(8)	6785(6)	58(1)
C(21)	10920(12)	1595(9)	6511(7)	52(1)
C(22)	118259(12)	1616(9)	6025(7)	58(1)
C(23)	12250(13)	2435(11)	5819(8)	80(1)
C(24)	11674(14)	3219(11)	6107(8)	94(1)
C(25)	10796(12)	3140(9)	6595(8)	64(1)
N(21)	10424(10)	2319(7)	6792(5)	49(1)
C(30)	10133(12)	900(9)	8921(7)	62(1)
C(31)	9872(12)	283(9)	9476(7)	61(1)
C(32)	9128(16)	529(9)	10004(7)	84(1)
C(33)	9041(17)	−44(11)	10492(8)	129(1)
C(34)	9334(14)	−919(10)	10415(8)	89(1)
C(35)	9997(13)	−1153(10)	9877(8)	77(1)
N(31)	10272(12)	−557(7)	9412(6)	71(1)

[a] $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* a_i a_j$.

polyhedron. Indubitably the strong distortion exhibited by the complex must be attributed to steric constraints caused by the pyridine groups present.

The coordination geometry of the title complex is similar to that found in the complex,[6] where copper(II) is bonded to the ligand 1,4,7,10-(2-pyridylmethyl)-1,4,7,10-tetraazacyclododecane. In the latter complex, a semi-coordinated bond was also present [the distance Cu–N(2) = 2.82 Å]. When the semi-bond is ignored, the intermediate between the square pyramid and trigonal bipyramid is also found, and the distortion towards trigonal bipyramidal geometry ($\tau = 0.42$) is similar to the present complex. In addition, the macrocycle of both the ligands takes a *trans-I* configuration in which all the lone

Table 3. Selected bond distances (in Å) and angles (in °).

Bond distances

Cu–N(1)	2.068(11)	N(2)–C(2)	1.559(20)
Cu–N(2)	2.144(14)	N(2)–C(3)	1.527(19)
Cu–N(3)	2.331(9)	N(2)–C(9)	1.452(21)
Cu–N(4)	2.828(10)	N(3)–C(4)	1.520(18)
Cu–N(11)	2.035(10)	N(3)–C(5)	1.469(16)
Cu–N(21)	2.037(11)	N(3)–C(20)	1.509(17)
N(1)–C(1)	1.471(16)	N(4)–C(6)	1.512(16)
N(1)–C(8)	1.564(19)	N(4)–C(7)	1.444(17)
N(1)–C(10)	1.470(17)	N(4)–C(30)	1.513(17)

Bond angles

N(1)–Cu–N(2)	83.0(5)	N(3)–Cu–N(21)	77.7(4)
N(1)–Cu–N(3)	119.5(4)	N(4)–Cu–N(11)	83.5(5)
N(1)–Cu–N(4)	74.5(5)	N(4)–Cu–N(21)	120.1(5)
N(1)–Cu–N(11)	79.8(4)	N(11)–Cu–N(21)	91.0(4)
N(1)–Cu–N(21)	162.0(4)	Cu–N(1)–C(1)	111.0(9)
N(2)–Cu–N(3)	81.5(5)	Cu–N(1)–C(10)	101.7(7)
N(2)–Cu–N(4)	124.9(6)	Cu–N(1)–C(8)	115.2(9)
N(2)–Cu–N(21)	94.2(5)	Cu–N(2)–C(2)	103.9(10)
N(2)–Cu–N(11)	141.7(5)	Cu–N(2)–C(3)	106.7(9)
N(3)–Cu–N(4)	67.5(6)	Cu–N(2)–C(9)	117.5(9)
N(3)–Cu–N(11)	136.5(4)		
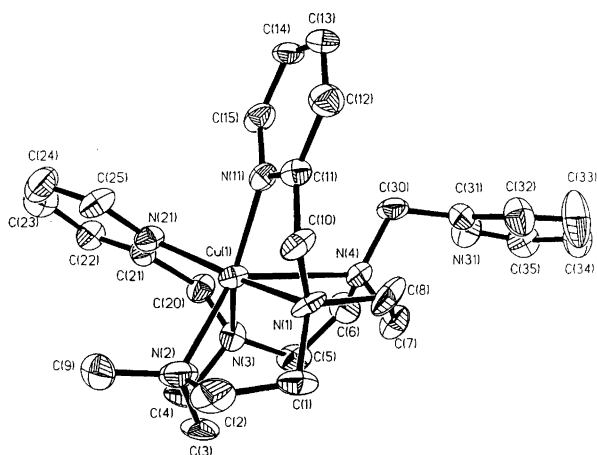
Fig. 1. ORTEP drawing with atom-labelling scheme of [CuL]$^{2+}$.

pairs in the four basal nitrogens are oriented to the same side of the macrocycle plane.[12] The macrocyclic ring is folding to coordinate to the metal ion, thereby relieving steric strain within the macrocycle and minimizing repulsion among the coordinated pyridine groups. In both the complexes, the copper atom is high above the mean plane formed by the four basal macrocycle nitrogens N(1), N(2), N(3) and N(4).

Spectral studies. The IR spectrum of the title complex shows vibration bands at 1609 and 1570 cm^{-1} assigned to the ν(py) vibration, and indicates that pyridyl groups

of L are coordinated to the metal center.[13] This is consistent with the results of the crystal structure analysis. In addition, vibrations of the counter-ion (perchlorate) at 1097 and 624 cm^{-1} are presented in the IR spectra.

The electronic spectrum of the complex (in methanol solution) shows a strong absorption band at 288(6.6) nm ($\varepsilon = 10^3 \, l \, mol^{-1} \, cm^{-1}$) which can be assigned to the intraligand transition. The spectrum of the complex also exhibits a broad peak (weak absorption) at 600–890 nm (maximum absorption at 695 nm, $\varepsilon = 140 \, l \, mol^{-1} \, cm^{-1}$) attributed to a d–d transition of the central copper(II) ion.

The ESR spectra of the title complex in DMF solution have been obtained at room temperature and at 110 K. The spectrum is split into four equally spaced absorptions by interaction with the copper(II) nucleus ($I = 3/2$) at 110 K. The solution spectrum does not present a similar hyperfine structure at room temperature. The phenomenon can be caused by the interaction with solvent. The ESR parameters deduced from the ESR spectrum (at 110 K) are $g_{\parallel}$ and $A_{\parallel} = 144$ G.

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